Journal of Positive School Psychology http://journalppw.com
2022, Vol. 6, No. 6, 7874-7881

Comparison Of Hydration Arresting Methods For Concrete Containing Supplementary Cementitious Materials

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Abstract

This research has compared various hydration stoppage methods like a solvent exchange, oven drying, and without arresting the hydration methodsfor the microstructure analysis results. This research has carried out the X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM) for the abovementioned methods. The concrete samples were extracted from the concrete pore after 28 days of curing and tested at 56 days for all the methods. The extracted sample was directly kept in the ventilated oven at 105 temperature in the oven drying method. Two solvents, isopropanol and diethyl ether were used to arrest the heat of hydration in the Solvent exchange method. These two methods were compared to the without arrested hydration samples with evidence of the microstructural analysis. It is concluded that the oven drying and solvent exchange methods remove the water, but the oven drying method damages the microstructural behavior of concrete. Microstructural results data indicate that the solvent exchange using isopropanol by diethyl ether is the most reliable method for the sample preservation for the removal of water in concrete samples.

Keywords: Cement, SCMs, Hydration Stoppage, XRD, SEM.

1. INTRODUCTION

Hydration stoppage is significant when studying the hydration of cement. Hydration stoppage is not only used for only storage of the sample before testing, but also it prevents reaction due to its capillary water. In addition, most of the microstructural analysis [16,17] techniques, such as Scanning Electron Microscopy, Thermogravimetric analysis, X-ray diffraction analysis, Mercury Intrusion porosimetry, etc.,are required dry samples to obtain accurate results.It is necessary to remove the capillary water from the sample because hydration of cement can not be stopped without extracting the water. Structural Water, gel water, and capillary Water are some of the types of water found in hydrated cement. Crystallization water and chemically bonded, non-vaporable water that can only be recovered via hydrate decomposition are types of structural water [1].

Many hydration stoppage methods use either a direct drying approach, in which water is evaporated directly from the sample or a solvent exchange approach. Free Water is first replaced by an organic solvent that is miscible with water and then evaporated to remove the solvent. Both techniques are widely used. Oven, vacuum, and freeze-drying are the three most prevalent methods of direct drying now available. Isopropanol, ethanol, methanol, acetone, and diethyl ether are a few solvents often exploited to inhibit cement hydration. Many distinct techniques are described in the literature for each approach or method [2]. It is difficult or impossible to remove water from a specimen without changing its microstructure and chemical content. Hence every method required some specimen alteration [3-5].

Direct drying (the removal of water by evaporation or sublimation) and solvent exchange methods are the most popular methods to stop hydration and removemoisture. This attempt compares the oven-drying and solvent exchange methods with the untreated or hydrated samples. These three samples were taken simultaneously, and the extraction of samples from the concrete for the microstructural study at the age of 28 days. Preventing the microstructure is challenging for the fresh cement paste, which contains a very high free water content. When conducting microstructural research on a concrete sample, it is critical to understand how to stop the curing process. Capillary tension and strong hydrogen bonds are used to keep gel water on the surface of the primary C–S–H gel.

2. MATERIALS

OPC 53 Grade cement, according to IS 12269-1987 [13], GGBFS and MF was used as binder materials in this study. The chemical properties of OPC, GGBFS, and MF are shown in Table 1. M30 grade of concrete was used in this experimental work.Here, a sample paste having 50% of Portland cement, 30% GGBFS, and 20% MF combination has been tested for three hydration stoppage methods. M30 grade of concrete was prepared according to IS 10262:2019[14] and cured these samples for 28 days in water curing. After 28 days of curing, samples have extracted from the specimen for SEM and XRD analysis for all these three methods. There are three ways to prepare the samples for testing. In the firstone, the samples remain the same or untreated. The different hydration stoppage methods have been applied for the second and third ways, and samples have been prepared accordingly. All microstructural tests have been carried out for all these three different samples at 56 days of concrete. Manufactured Sand confirming Zone-II grading as per IS383:2016 [15] was used as a fine aggregate (FA). Coarse Aggregate (CA) and FA areused locally in this experimental work.

Table 1 Chemical Properties of OPC, GGBS and Micro Fine

Particulars	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	SO_3
Cement	**63**	**20**	**6**	**3**	**1.5**	**0.5**	**0.5**	**2**
GGBS	**38.09**	**32.19**	**8.59**	**2.8**	**5.5**	**0.26**	**0.4**	**8.89**
Micro Fine	**36.7**	**35.1**	**17.58**	**1.62**	**7.75**	**NA**	**NA**	**0.65**

NA: Oxide content was not found or not available

3. METHODS

In this research article, there are mainly three methods: selecting the hydration of the concrete using supplementary cementitious materials for the stoppage.

1. Oven drying method
2. Solvent exchange method and

3. Sample collecting and rest in zipping lock airtight plastic bag

Oven drying method:

In this method, the mass of the sample has to take at each 2 hours interval [5]. Until and unless the subsequent sample weight will not be the same, the process will be continued. The oven-drying process is an excellent way to evaporate the embedded water, but it damages the microstructure of the concrete at 105 ℃ [6]. There are two types of water present in the concrete sample. At 105 ℃, the water will be evaporated from the concrete pores, but at this temperature, the nonevaporated water will also evaporate from the ettringites and C-S-H gel, creating the fragile microstructure [7].

Moreover, the weight loss of the sample is higher at 580 to 710 ℃ in TGA because evaporation of CO_2 from calcite [8]. Beaudoin claims that drying for 3 hours at 105 ℃ causes less microstructural damage than drying for 24 hours [9]. In addition to capillary pressure damage, microcracking in mortar and concrete can be caused by the differential thermal expansion of aggregates and hardened cement paste during drying. During evaporation, there is a chance of damaging concrete microstructure by the capillary pressure of the water vapor because the gases form of water creates the thermal expansion of concrete ingredients [10].

Solvent Exchange Method:

Many types of solvents are used to remove the water from the concrete samples. An ideal solution with the smallest molecular size can be used to replace the smallest pores of water. So, it can easily penetrate the place of the capillary water. This solvent's boiling temperature should be lower than the water. In order to remove the solvent without damaging the cement's structure and composition, a lower boiling point (higher vapor pressure) is preferable. The solvent must be water-miscible to stop the hydration and replace the water in the pores. Using a fast-dissolving solvent in water may effectively stop the hydration of a substance. It is possible to decrease pore structure damage during drying by reducing water surface tension.

After the emergence of the sample, it has to monitor the weight of the sample atan interval of 24 hours. If the weight of the sample should be stabilized,the sample has to be removed from the solvent at an elevated temperature. The samples were collected from the solvent using a basic filter, and the sample was washed once with isopropanol and twice with diethyl ether. The sample was kept in an oven at 40 ℃ for 8 minutes at atmospheric pressure. The granular particles of samples were stored in a low vacuum desiccator over silica gel until further analysis.

Solution-to-sample ratio

As per the literature survey, there is a different sample to solution ratio taken by all past researchers [10-12]. Aligizaki et. [10] al suggests that the solution to sample volume ratio is 100:1. Another author, Day and Marsh [11], used solvent to pore water is 500:1, and Beaudoin [12] took 100:0.003 solvent to solid ratio. So, in this case, no need to renew the solvent frequently. It is concluded that when the user takes the higher solution to sample ratio, there is no need to change the solution frequently.

Sample collecting and rest in zipping lock airtight plastic bag

In this method, the extracted samples for XRD and SEM must be put directly in the desiccator without any treatment. Some of the researchers have done this before the testing of microstructural analysis. In addition, the extracted samples were kept in the zipping bag without any process, as shown in Figure 1.

4. EXPERIMENTAL

4.1 Sample Preparation for Microstructural Studies

For the sample collection for the SEM analysis, a sample size should not be more than 10 mm, and most of the mortar and aggregate parts must be visible. Same in the XRD sample, the particle size diameter should not exceed 75 microns. Grind the sample using a special hammer and shell to make XRD powder. The final sample has been stored in a zipping lock bag and kept in a desiccator. Silica-Gel is used to absorb the atmospheric water in the desiccator. Several tests such as Scanning Electron Microscopy Images (SEM),

X-ray diffraction (XRD), Energy Dispersive Spectroscopy (EDS), Thermotropic Analysis (TGA), and Fourier Transform Infrared Spectroscopy (FTIR) were performed to evaluate the microstructural properties.In conjunction with SEM (FE-SEM, ZEISS equipment, Germany), INCA software was used to conduct SEM analysis. For XRD, a sample was determined using D8 advanced X-ray powder diffraction equipment and installed the sample rack on the instrument platform with 3-4 g of the prepared sample. Samples were scanned between 5° to 65° (2θ) in continuous mode with an integrated step scan of 0.02° per second. Match-3 software was used to identify the presence of minerals in the provided sample.

4.2 Solvent Exchange Method (Method A)

The specimen was initially weighed and then immersed in an organic liquid during the solvent exchange. Isopropanol (AR grade) was taken as the organic liquid and chosen as a solvent in this research. Particles become saturated with solvent as soon as they're submerged in water. The change in mass of the specimen is used to monitor solvent penetration, and it takes 7-10 days to stabilize the weight of the samples. That different solvent has removed isopropanol with a lower boiling point than the first one. This research uses diethyl ether to remove isopropanol molecules from the concrete pores, as shown in Figure 2.

4.3 Oven Drying Method (Method B)

The oven-drying method is the most widely used method to stop the hydration in cement paste. In this method,the temperature should be 65 to 105ºC at atmospheric pressure. Drying is considered complete while the sample reaches a constant mass (commonly less than 0.1% of each day mass alternate).The oven-drying technique is executed in a ventilated and temperature-programmed oven. Drying periods have been selected: oven-drying at 105ºC for 3 hrs and oven-drying at 105ºC for 24 hrs. Oven-drying at 105ºC for 24 hrs is the most suitable method for removing the complete non-bound water.Oven-drying at a lower temperature is not selected in this experiment because it will take more time to evaporate water. At that time, the hydration of cement will be carried out, and the microstructural analysis result will be misleading. Galle [8] found that Ettringite and C–S–H lost massive non-evaporable water at 105 °C.

4.4 Without Hydration Stoppage (Method C)

The extracted sample from the concrete cube is directly stored in the desiccator without any treatment, as shown in Figure 1. The extracted sample have stored in the zipping bags and kept in the desiccator without any treatment. The samples were tested for microstructural analysis after 28 days of extraction.

Figure 1. Sample packed in zipping lock bag

Figure 2. Solvent exchange method

5. RESULTS AND DISCUSSION

SEM and XRD tests have been performed for above mentioned various treatments of hydration stoppage. Here, the M30 grade of concrete, consisting of 50% of cement, 30% of GGBFS, and 20% of MF, has been used to investigate the

microstructural properties with different hydration stoppage methods.

5.1 SEM analysis

SEM (Scanning Electron Microscopes) analysis has been carried out for the abovementioned samples. As discussed in section 4, three hydration stoppage methods have been incorporated to compare the microstructural behavior of SEM. Figure 3 and Figure 4 represent the SEM image of hydration stoppage by solvent exchange and oven drying method, respectively. Moreover, it is visible that while comparing the crack width of the microcracks in both images, oven drying samples' crack width is wider as compared to that of solvent exchange methods sample. The synergetic effect of the evaporation of water held in capillary pores and thermal expansion of the concrete ingredients in the oven drying method results in micro-crack formation and an increase in the width of existing cracks in concrete samples.While in the solvent exchange method, the samples were submerged in solvents at ambient temperature.

Further, removing the second solvent, the sample was kept in a ventilated oven at 40° Ctemperature only. Therefore, no thermal expansion takes place in the solvent exchange samples. Figure 5 and Figure 6 show the SEM images of the solvent exchange method and without the hydration stoppage method. It is noted that the heat of hydration has stopped in the sample influenced by the solvents because only C-S-H gel formed due to the initial heat of hydration of cement. After 28 days, samples were immersed in a solvent, and water pores were replaced by the solvent used in this method. Ultimately, the heat of hydration has stopped due to the absence of water in concrete pores. The samples unarrested for hydration experienced a continuation of the heat of hydration due to the presence of water in pores, and water plays a vital role in secondary reaction [17]. Therefore, the supplementary cementitious material creates the secondary heat of hydration in the presence of C-S-H gel, creating a sheet-shaped AFm.

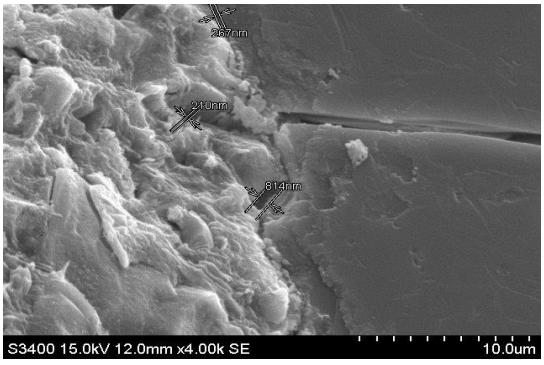


Figure 3 SEM image of Method A

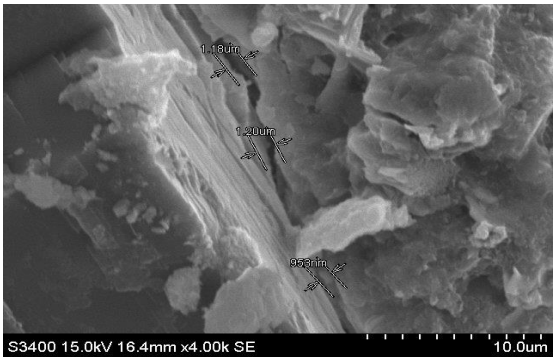
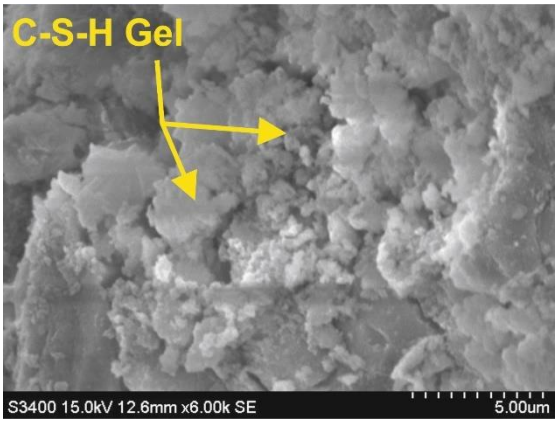


Figure 4 SEM image of Method B



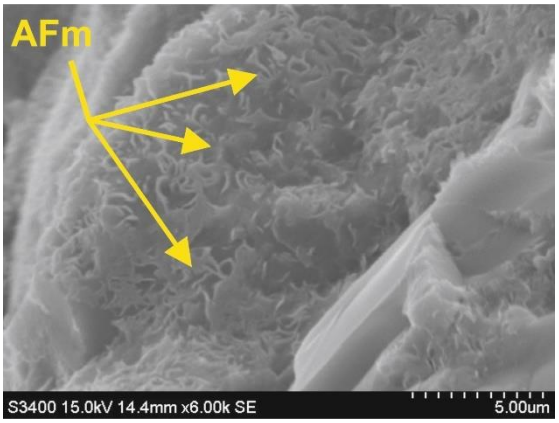


Figure5 C-H-S gel formation at 5 microns in method A

Figure6 C-H-S gel formation at 5 microns in method C

5.2 XRD (X-ray Diffraction) analysis

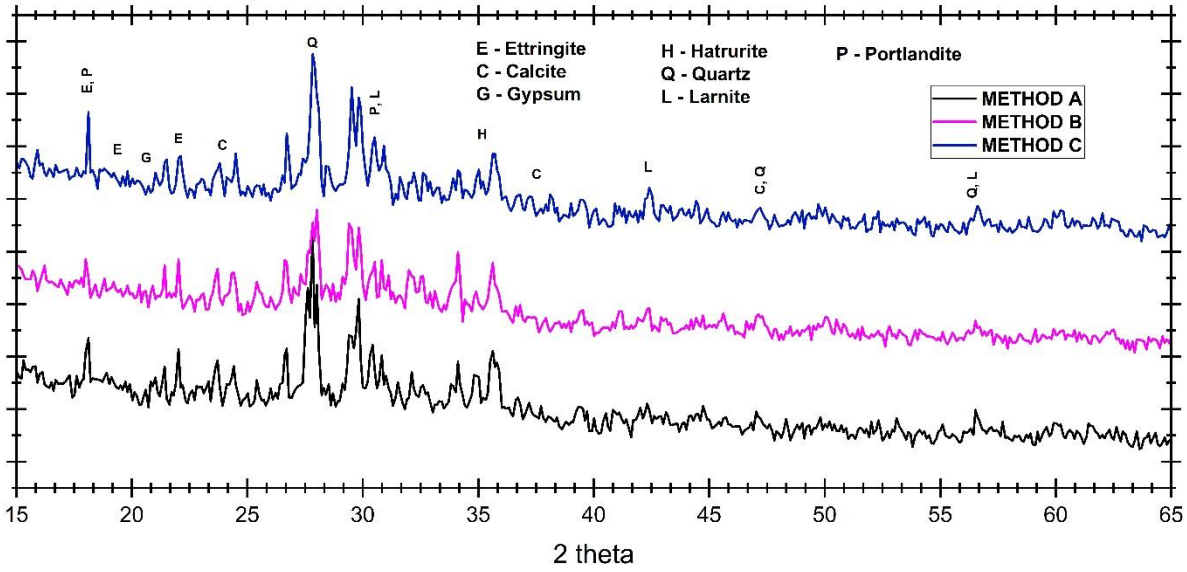


Figure 7 XRD graph of Method A, B, and C

XRD (X-ray Diffraction) analysis has been carried out to find the different minerals in the concrete samples.Here, three different methods for hydration stoppage method have been incorporated, as discussed earlier. Figure 7 shows the XRD analysis for methods A, B, and C. it is visible that the lesser peak intensity for ettringites and calcite in the solvent exchange and oven drying samples compared to the untreatedsample (Method C). It indicates that the solvent exchange and oven drying methods have removed the pore water content. The heat of hydration could not occur without water, and the reaction stopped due to the unavability of water content in the concrete sample.

Moreover, the peak intensity of all the minerals seems higher in the untreated sample. In addition, larnite is responsible for long-term strength gain in the concrete sample [ ]. It is found to be higher in method C. It shows that the heat of hydration has been continued during the sample preservation in the desiccator. Furthermore, while comparing the peak intensity of methods A and B, ettringites and portlandite are lower in the oven drying sample because a higher degree of temperature damages the formation of C-S-H gel and ettringites in concrete samples.

6. CONCLUSIONS

In this research, SEM and XRD tests have been incorporated into this research to identify the ideal method for arresting the hydration of cement containing different SCMs in concrete. As mentioned earlier, the three different methods have been assessed and compared. After a detailed analysis of XRD and SEM following conclusions can be drawn:

1. The heat of hydration continuously increases while the sample is kept as it is (method C). after extracting the testing sample, the formation of C-S-H gel remains continuous with time. It leads to a change in microstructure analysis results due to capillary water reacting with the binder content in the concrete sample.
2. The oven-drying method at 105^{o}C for 24 hours not only removes the water from the concrete sample but also damages the concrete microstructure. Because of the concrete sample's thermal expansion, the existing microcracks get wider and generate new microcracks. Therefore, the

oven drying method is not suitable for microstructure analysis.

3. In the solvent exchange method, the solvents remove the water from the concrete pores and prevent the water stored in C-S-H gel and ettringites. Moreover, it does not damage the microstructure of concrete samples.

After the meticulous analysis of the hydration arrested methods, it has been concluded that the solvent exchange method is best in terms of sample preservation for microstructural analysis.

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